COATINGS

PHASE COMPOSITION AND STRUCTURE
OF DULL LOW-MELTING GLAZES

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The possibility of producing dull low-melting glazes for ceramic products to be fired according to a slow firing regime based on the system $Na_2O – MgO – CaO – B_2O_3 – Al_2O_3 – SiO_2$ is demonstrated. The results of studying glaze glasses and coatings by x-ray phase analysis, electron microscopy, infrared microscopy, etc. are described. A correlation between the structure and the phase composition of coatings and their qualitative characteristics is established. The main properties of synthesized dull glazes are specified.

Household majolica and pottery are becoming increasingly popular. Producers appreciate the possibility of using inexpensive local argillaceous materials, whereas consumers appreciate high artistic qualities reviving the traditions of folk crafts. Dull glazes used for decorating majolica products impart diverse types of textures to the majolica surface and conceal the heterogeneity in color tones that is typical of majolica. Furthermore, a glaze coating can improve the service properties of an article and decrease its disadvantages, such as high porosity, high water permeability, and low mechanical strength.

One of the best methods for obtaining a dull glaze surface is based on inducing a crystalline phase in the coating, whose refractive index differs significantly from that of the matrix glass. The dullness of such coating is determined by the diffuse reflection of light from the faces of the emerging crystals, and the degree of dullness depends mainly on the size and quantity of crystals.

The development of glazes not containing expensive or toxic components is of special interest. The research in the synthesis of opaque zirconium-free glazes performed at the NIIstroikeramika Institute [1] and at the Kharkov State Polytechnic University [2], as well as our studies [3], indicate that glaze coatings with a dull texture can be obtained in the system $R_2O – RO – B_2O_3 – Al_2O_3 – SiO_2$ [R_2O) Na_2O, K_2O; RO) MgO, CaO] due to the formation of opacifying phases represented by wollastonite and diopside under optimum temperatures. According to the authors of [1, 3], a silky-dull coating surface can be ensured by the formation of a finely

dispersed structure with crystal sizes not more than 10 μm. However, the known compositions are intended for construction ceramics whose technology involves fast firing.

The purpose of the present study is to obtain dull glazes based on the system $Na_2O – MgO – CaO – B_2O_3 – Al_2O_3 – SiO_2$ by a slow-firing regime, which would be formed due to the crystallization processes.

For our study we selected a range of compositions containing a constant quantity of Na_2O and Al_2O_3 equal to 10 and 3%, respectively (here and elsewhere mol.%, unless otherwise specified). The following contents of the components were studied (%): $0 – 10.0$ MgO, $2.5 – 22.5$ CaO, $4.5 – 19.5$ B_2O_3, and $50.0 – 65.0$ SiO_2.

Experimental glaze glasses were obtained by melting batches whose components included quartz sand, boric acid, soda ash, chalk, dolomite, alumina, and magnesia. Synthesis was performed in a gas furnace at $1450 – 1530°C$ for $6 – 7$ h with a 1 h exposure at the maximum temperature. The glasses have satisfactory melting and working properties, and the majority of them are transparent and have a greenish shade. Glasses containing 19.5% B_2O_3 become opalescent in working. The x-ray phase analysis established that most experimental glass are x-ray-amorphous. Differential-thermal analysis of the glasses indicated the presence of two endothermic effects extended in the temperature interval of $600 – 730°C$, whose presence is typical of liquating glasses. The inflections visible in the DTA curves are related to two temperatures, i.e., vitrification and softening, which indicates the presence of two vitreous phases [4]. Crystallization is indicated by the exothermic effects at temperatures of $815 – 980°C$ observed in most compositions.

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Electron microscopy study of the glass structures performed by the replica method after pickling a fresh fracture with 2% HF for 3 or 5 sec identified liquation predominantly of the drop type. The introduction of MgO instead of CaO facilitates the phenomenon of secondary stratification. As MgO content grows from 5 to 10%, the size of larger drops grows from $0.1 - 0.2$ to $0.3 - 0.6$ μm; at the same time the quantity of drops in a unit volume decreases. Secondary drops have a size not more than $0.05 - 0.10$ μm. In compositions with a constant content of CaO equal to 15%, an increasing quantity of MgO from 2.5 to 10.0% is accompanied by the transition from a two-skeleton liquation structure to a drop structure followed by an insignificant enlargement of drops to 0.2 μm and their growing quantity.

In our experiment we established the propensity of most glaze glasses for crystallization in the temperature interval of 750 – 1050°C. The presence of magnesium and calcium oxides activates the crystallization process under the thermal treatment of the considered glasses. A rather high crystallization capacity of glaze glasses under heat treatment makes them suitable for producing glaze coatings with a crystalline structure.

The samples of coatings were prepared by the traditional method. A glaze slip was produced by the moist milling of initial glass adding $5 - 10$ wt.% (above 100%) refractory clay milled to a residue of $0.3 - 0.5$% on a No. 0063 sieve. This suspension was applied to prefired ceramic articles made of low-melting local clays with water absorption equal to $18 - 20$%. The CLTE of the ceramic substrate was $(72 - 78) \times 10^{-7}\,K^{-1}$. The experimental samples were fired in electric furnaces in a temperature interval of $950 - 1000$°C with an exposure at the maximum temperature for 1 h.

Based on glaze fusing results, the ranges of formation of a dull texture have been determined and the optimum-quality dull coatings containing up to 10% MgO and $5 - 20$% CaO have been identified.

According to x-ray phase analysis data, the phase composition of dull coating is represented by several crystalline phases: wollastonite, pseudowollastonite, diopside, and cristobalite. The coatings containing not more than 5% MgO have the most complex phase composition. They are characterized by a redistribution of the existing crystal phases as the quantities of MgO and CaO in the mixture vary. Analysis of the dependences of the relative intensity of diffraction maxima corresponding to particular crystal phases in the coatings suggests the following conclusions. As the MgO content grows to 5%, the quantity of pseudowollastonite, wollastonite, and cristobalite decreases the most intensely. With MgO equal to $5 - 10$%, in addition to the above, diopside is crystallized and its quantity grows with increasing MgO content. Diopside is the prevailing phase for the coatings bearing 7.5 and 10.0% MgO. Within the composition ranges with a constant content of MgO (5.0, 7.5, or 10.0%) the quantity of diopside grows until the content of CaO in the composition exceeds $1.2 - 1.4$ times the content of MgO.
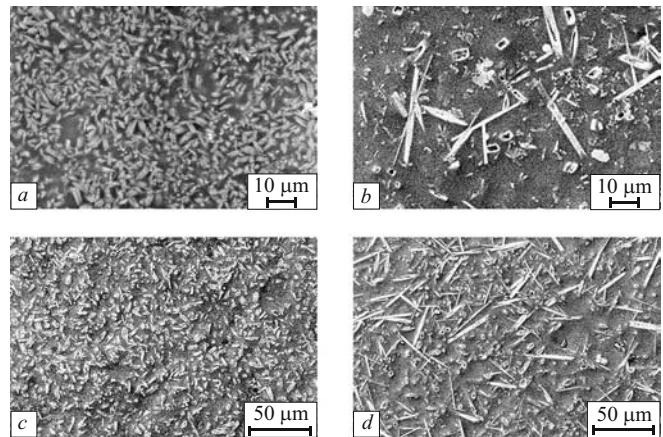

Fig. 1. Electron microscope photos of glaze coatings with different textures: *a*) semidull diopside-bearing; *b*) silky-dull containing wollastonite and diopside; *c* and *d*) intensely dull containing diopside or wollastonite, respectively.

Upon a further increase in the content of CaO, the Ca^{2+} cations that have not been used in the formation of diopside presumably saturate the glass matrix and participate in the formation of wollastonite crystals.

As for the surface of the coatings considered, one of the reasons for the increasing dullness in the samples with luster up to 16% is the increasing volume of the crystalline phase. This agrees with the published data [1, 3]. Analyzing the results of x-ray phase analysis, it can be assumed that the formation of a dull surface in compositions not containing MgO is mainly due to the formation of pseudowollastonite and wollastonite crystals in firing, as well as cristobalite, whose quantity decreases when CaO is introduced instead of SiO_2. The slight increase in the luster of the coatings considered with a minimal MgO additive (2.5%) is related to the decrease in the total volume of crystal formation. The decreasing crystallization capacity of glaze coatings correlates with the gradient crystallization of the initial glaze glasses. The dullness of coatings containing over 5% MgO is mainly due to the crystallization of diopside.

It is interesting that dull coatings with a high content of crystalline phases have been synthesized not only based on glaze glasses prone to crystallization when heat-treated in the solid state, but also based on glasses that do not crystallize under such conditions. The reason is probably the following. The powdered state of the glaze applied to a ceramic substrate facilitates the crystallization of coatings under firing due to the emergence of a highly extended surface in glass particles. Furthermore, crystallization is stimulated by the gas bubbles adsorbed on the surface.

The structure of dull coatings was studied with a JSM-5610 LV electron microscope (Japan). It was established that the coating texture depends not only on the quantity of the specified crystalline phases, but also on the size and shape of their crystals (Fig. 1). Semidull coatings whose luster reaches $45 - 50$% have fine crystals, not larger than
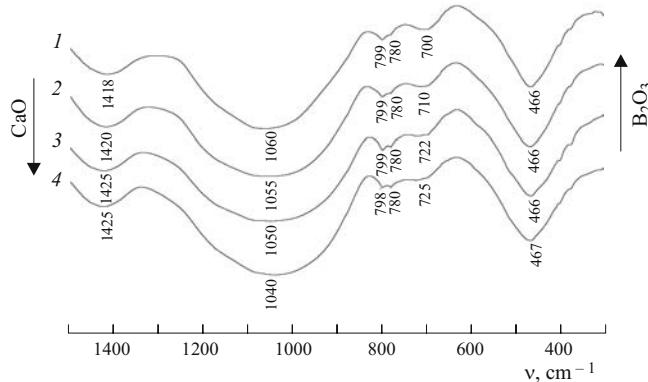
Fig. 2. IR spectra of initial glasses with constant quantities of MgO (7.5%) and SiO$_2$ (55.0%). Content of CaO and B$_2$O$_3$, respectively (%): *1*) 7.5 and 17.0; *2*) 10.0 and 14.5; *3*) 12.5 and 12.0; *4*) 15.0 and 9.5.

6 – 8 μm, with fused faces. The silky-dull texture (luster 27 – 35%) typically has a fine-crystalline structure represented mainly by short prismatic crystals of size up to 8 × 4 μm and small tabular crystals up to 12 × 3 μm uniformly distributed over the surface. Less frequently large prismatic crystals of size around 15 × 4 μm and tabular crystals of size 38 × 4 μm are found. The structure of intense dull coatings (luster 16 – 22%) is represented by large tabular crystals, on the average 20 – 40 μm long and 0.8 – 4.6 μm wide, or prismatic crystals ranging from 4 to 10 μm in the diagonal. Crystals in dull coatings have clearly expressed faces. It should be noted that coatings containing diopside have good spreading over the surface. This property of dull glazes can be attributed to the high dispersion of the emerging diopside phase, which activates the opacification.

Comparing the microphotos of glaze coatings containing (%): 2.5 MgO, 15.0 CaO, 14.5 B$_2$O$_3$, and 55.0 SiO$_2$ produced in the temperature interval of 950 – 1000°C we have registered the growth of crystals with increasing temperature. As the same time the crystals acquire a better defined habitus and their number decreases. It can be assumed that the temperature of 1000°C is more favorable for the formation of these crystals identified by x-ray phase analysis as wollastonite. As the firing temperature increases, the microhardness of the glaze coatings grows from 7480 to 8030 MPa. Thus, a certain ordering takes place in the structure of the glaze coating with increasing firing temperature, which has a positive effect on its strength parameters.

Some necessary additional data on the structure of glaze glasses and coatings were obtained by a systematic infrared spectroscopy study. The IR spectra of glaze glasses (some of then are shown in Fig. 2 as examples) have wide absorption bands with maxima at 1418 – 1425, 1040 – 1082, and 465 – 468 cm^{-1}.

The main absorption band in the range of 1100 – 1010 cm^{-1} indicates the presence of silicon-oxygen groups with different degrees of polymerization [5]. A comparison of IR spectra of compositions with different CaO contents reveals the shift of the main absorption band (1063 – 1060 cm^{-1}) toward lower frequencies (1040 cm^{-1}), as the CaO content increases. This suggests a depolymerizing effect of calcium cations on the silicon-oxygen tetrahedrons, which should facilitate the transition from a skeleton structure to a chain structure. Analysis of the effect of MgO on the glaze glass structure yields similar results. Some fluctuations are observed in the position of the main absorption band as the content of MgO in the glasses varies from 0 to 7.5% (replacing B$_2$O$_3$). However, the general trend is the main band maximum shifting toward the lower-frequency range with increasing MgO content, which points to the decreasing degree of cohesion of [SiO$_4$] groups. Replacing CaO by MgO does not affect the position of the main band maximum.

An absorption is registered near 1420 cm^{-1} in the high-frequency spectrum range, which can be attributed to the vibrations of three-coordination boron in the complex with polymerized groups [BO$_3$] [6]. The absorption bands in the range of 625 – 750 cm^{-1} point to the nonplanar deformation vibrations of the bonds B(III) – O – B(III) [7]. An increase in the content of CaO from 5.0 to 15.0% and MgO from 0 to 7.5% causes a shift of these absorption band maxima to a higher-frequency range, which may be evidence of an increased number of polymerized boron groups.

The rather intense band at 465 – 468 cm^{-1} is due to the asymmetric deformation vibrations in the tetrahedrons [SiO$_4$] [8]. It is difficult to identify the presence of four-coordination boron based on the available IR spectra in view of a possible superposition of the similar frequencies that are characteristic of [BO$_4$] groups and vibrations of the Si – O bond [8, 9]. Mutual substitution of magnesium and calcium oxides does not perceptibly modify the IR spectra of glasses.

Thus, the IR-spectroscopy study of the x-ray-amorphous glaze glasses has identified the formation of seed groups emerging in the precrystallization period.

Substantial structural transformations occurring in glaze glasses as a consequence of thermal treatment are reflected in the IR spectra of the coatings fired at 1000°C. Some of these spectra are shown in Fig. 3. The absorption bands at 1418 – 1425 cm^{-1} typical of the vibration of three-coordination boron in a complex with polymerized groups have shifted toward lower frequencies (1400 – 1417 cm^{-1}) and have become smoother. Hence it can be concluded that the thermal treatment of samples decreases the degree of polymerization of these groups and decreases the number of three-coordination boron atoms.

The modifying cations have slightly different roles in the structures of coatings and initial glasses. An increase in the amount of CaO decreases the intensity of the absorption band near 1400 cm^{-1}. Comparing the spectra of coatings with different contents of MgO, it can be noted that this oxide does not have a perceptible effect on the positions of the characteristic bands of [BO$_3$] groups. However, similarly to CaO and MgO, it decreases the intensity of the respective band.

The main absorption band on IR spectra of coatings, which is responsible for the vibrations of silicon-oxygen tetrahedrons, is shifted toward higher frequencies compared to the initial glass and becomes somewhat narrower. The position of this band maximum at $1078 - 1090$ cm^{-1} is typical of ring, ribbon, or chain silicates with interrelated groups. The band in the range of $700 - 725$ cm^{-1} disappears; furthermore, new absorption bands emerge with maxima at $514 - 515$, 635, 673, $872 - 876$, $923 - 926$, and $986 - 995$ cm^{-1}.

The splitting of the absorption band in the frequency interval of $800 - 1000$ cm^{-1} into several low-intensity components may point to a structural regrouping, where the silicon-oxygen skeleton breaks under the effect of the modifier cations in the course of formation of new metasilicate groups. The absorption intensity grows when CaO is replaced by MgO, which presumably indicates an intensified crystal formation. At the same time, the general increase in the microhardness of investigated coatings regularly increases with increasing MgO : CaO ratio. The microhardness for glaze coatings varies from 5600 to 8330 MPa. Additional bands at $900 - 926$ cm^{-1} may indicate either the formation of nonbridge bonds $Si(IV) - O^-$, or the presence of BO_4 groups [8].

An absorption is registered in the low-frequency range near 500 cm^{-1} due to the inner deformation vibrations of the tetrahedron $[SiO_4]$, whereas the insignificant increase in the frequencies of theses vibration compared to free anions $[SiO_4]^{4-}$ is due to the lattice vibrations of the new silicate formations, i.e., bonds with participation of Ca^{2+} and Mg^{2+} [8].

The spectra of glaze coatings containing $5 - 10\%$ MgO have two typically recurrent absorption maxima at 673 and 635 cm^{-1}, whose intensity grows as the CaO content increases (instead of SiO_2 or B_2O_3) or in the equimolar replacement of CaO by MgO. These frequencies can be attributed to the symmetric vibrations of $Si - O - Si$ in the diopside lattice [8]. The presence of three absorption bands in the interval of $550 - 700$ cm^{-1} (around 566, 645, and 695 cm^{-1}) in the spectra of the compositions containing less than 5% MgO is typical of the valence vibration of three $Si - O - Si$ bridges that form an elementary link in the metasilicate chain of wollastonite.

Most spectra have doublet bands with maxima at 780 and 800 cm^{-1}, which are characteristic of quartz that may be present in small quantities in the form of unmelted particles. The absorption in this range with a single maximum is registered, for example, in the spectra of the coatings that contain (%): up to 2.5 MgO, 12.5 CaO, $12.0 - 14.5$ B_2O_3, and 60.0 SiO_2 and is responsible for other modifications of silica.

A comparison of the IR spectra of the initial glaze glasses and coatings synthesized on the basis of these glasses shows that substantial changes occur in the glass structure as a result of thermal treatment. In view of several components present in the specified system, it is difficult to uniquely interpret the position of the absorption bands. The identification of individual groups is hampered by the superposition of several characteristic absorption bands. However, the de-
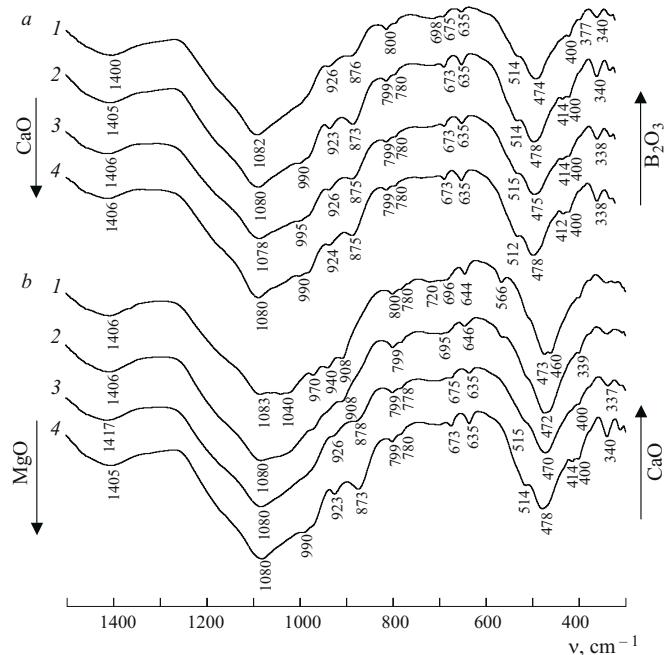
Fig. 3. IR spectra of glaze coatings: *a*) with constant content of MgO (7.5%) and SiO_2 (55.0%) and the contents of CaO and B_2O_3, respectively (%) [*1*) 7.5 and 17.0; *2*) 10.0 and 14.5; *3*) 12.5 and 12.0; *4*) 15.0 and 9.5]; *b*) with constant content of B_2O_3 (14.5%) and SiO_2 (55.0%) and the contents of MgO and CaO, respectively (%) [*1*) 0 and 17.5; *2*) 2.5 and 15.0; *3*) 5.0 and 12.5; *4*) 7.5 and 10.0].

crease in the absorption intensity in the range of $1400 - 1450$ cm^{-1} and the disappearance of the maxima at $700 - 725$ cm^{-1} may indicate a decreased quantity of three-coordinated boron in its partial transition into the four-coordination state, considering the emergence of the respective absorption bands after heat treatment. Calcium and magnesium oxides facilitate the coordination transition of $[BO_3]$ to $[BO_4]$ by easily releasing their oxygen ion to boron. The differentiation of the IR spectra shows that liquation phenomena take place in the initial glasses, whereas crystallization processes occur in the coatings. This agrees with the data of DTA, x-ray phase analysis, and electron microscopy.

The presence of absorption bands of a certain nature in the frequency interval of $500 - 1000$ cm^{-1} makes it possible to identify chain groups of the $[(SiO_3)_n]_\infty$ type related to metasilicates in the coating. The IR analysis together with x-ray phase analysis makes it possible to identify a complex composition of the crystal phase of the glaze coatings, in which either wollastonite or diopside prevail depending on the chemical composition.

The study has determined the compositions of dull low-melting glazes fired according to the slow-firing regime, which are recommended for application in the production of ceramic construction and household products. The luster of optimum glazes is $16 - 40\%$, their whiteness $52 - 72\%$, microhardness $5600 - 8330$ MPa, thermal stability $8 - 18$

thermal cycles, and CLTE $(62.2 - 75.7) \times 10^{-7}\,K^{-1}$. The use of the new glazes opens new opportunities for expanding the product range and lowering its production cost.

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